5. RECOVERY OF ZIRCONIA FROM ZIRCON SANDS

The use of zirconia in many fields has grown enormously. The major and cheapest source of zirconia is zircon sand. Despite this, the decomposition of zircon is not easy to achieve due to its stability. Considering the structure of zircon, which is extensively discussed in the literature [3, 9, 10, 16, 47], this stability is quite understandable. Various methods of decomposition have been investigated owing to the different levels of purity required and the cost of manufacture. All these methods have three steps in common. Firstly, zircon is decomposed or dissociated by chemical, thermal or mechanochemical means. Secondly, the products obtained are treated by solubility differentiation. Thirdly, the zirconium compounds are isolated from the residual impurities.

5.1 Thermal Dissociation

The reaction is conducted in an arc plasma furnace that forms zirconia in droplets of silica. To avoid recombination or to reduce it to minimum levels, the mixture must be quenched rapidly. As a result, it produces crystals of zirconium oxide in amorphous silica. Further leaching with sulphuric acid is necessary to produce a zirconium sulphate solution and insoluble silica [12]. For leaching, sodium hydroxide can also be used. In this case, aqueous sodium silicate and zirconia are obtained. Sodium silicate is a useful by-product, which therefore can be commercialised. This process is environmentally friendly [2, 12].

In other processes, zircon is decomposed in an arc furnace at 2 000 °C. Silicone monoxide is generated, which re-oxidises to silicone dioxide outside the furnace [2, 16].

5.2 Decomposition by Fusion

The fusion procedure is very common in the recovery of zirconia from zircon sands. In this procedure, different fondants can be used. These include sodium hydroxide, sodium carbonate and calcium carbonate [12].

5.2.1 Fusion with sodium hydroxide

This is the well-known and usual method. Fusion is conducted at 650 °C with a slight excess of sodium hydroxide. In the formal process, the products of fusion obtained are sodium zirconate and sodium metasilicate or orthosilicate, depending on the mol ratios of alkali. The cooled reaction products are crushed and leached with water. As a result, sodium metasilicate is dissolved and sodium zirconate is hydrolysed to hydrous zirconia. Hydrous zirconia is insoluble and is recovered by filtration [2, 12, 15, 48].

$$ZrSiO_4 + 4NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2\ H_2O$$
$$ZrSiO_4 + 6NaOH \rightarrow Na_2ZrO_3 + Na_4SiO_4 + 3\ H_2O$$

Scheme 5.1: Reaction of zircon decomposition with sodium hydroxide by fusion, with high stoichiometric ratios [2]

$$Na_2ZrO_3 + xH_2O \rightarrow NaOH_{(aq)} + ZrO_2.xH_2O$$

Scheme 5.2: Reaction of hydrolyses of sodium zirconate

Recovered hydrous zirconia is fired and dissolved in mineral acids, which leads to the formation of various aqueous zirconium compounds that differ according to the mineral acid used [2, 12, 15, 48].

If the fusion is conducted with an insufficient amount of sodium hydroxide, sodium zirconium silicate is obtained as a major product.

$$ZrSiO_4 + 2NaOH \rightarrow Na_2ZrSiO_5 + H_2O$$

Scheme 5.3: Reaction of zircon decomposition with sodium hydroxide by fusion, with low quantities of sodium hydroxide [2]

Na_2ZrSiO_5 is insoluble in water and therefore requires acid treatment to dissolve the cake [2, 12, 48].

5.2.2 Fusion with sodium carbonate

For this fusion, temperatures must be higher than 1 000 °C. In contrast to sodium hydroxide fusion, the compound of zirconium obtained is sodium zirconium silicate, which is water-insoluble, being soluble only in acid. Strong acids therefore have to be used to dissolve it. The common process uses hydrochloric acid [12].

$$ZrSiO_4 + Na_2CO_3 \xrightarrow{1000^\circ C} Na_2ZrSiO_5 + CO_2$$

$$Na_2ZrSiO_5 + 4HCl \longrightarrow 2NaCl + ZrOCl_2 + SiO_2 + 2H_2O$$

Scheme 5.4: Reaction of zircon decomposition using sodium carbonate as fondant, with subsequent treatment with hydrochloric acid [2]

At high ratios of sodium carbonate, sodium zirconate and sodium silicate are also formed. This can be explained by the following reaction equation [2]:

$$Na_2ZrSiO_5 + Na_2CO_3 \rightarrow Na_2ZrO_3 + Na_2SiO_3 + CO_2$$

Scheme 5.5: Reaction of zircon decomposition using sodium carbonate as fondant, with low amount of sodium carbonate [2]

5.2.3 Fusion with calcium oxide and magnesium oxide

With calcium oxide, calcium zirconium silicate, calcium zirconate and calcium silicate are produced. A mixture of zirconium dioxide and calcium or magnesium silicate can also be produced. The products are dependent on the mol ratio of the reactants and on the temperature of the process [2, 49].

$$ZrSiO_4 + CaO \xrightarrow{1100^\circ C} Ca_2ZrSiO_5$$

$$ZrSiO_4 + 2CaO \xrightarrow{1600^\circ C} Ca_2SiO_4 + ZrO_2$$

Scheme 5.6: Reaction of zircon decomposition with calcium oxide, with two different mol ratios [2, 49]

Magnesium oxide is the most suitable fondant for the reaction using the alkaline earth oxides, because of its high solubility and its almost negligible rates of hydration and carbonation. It is available in nature in the form of the mineral periclase [49].

5.2.4 Fusion with potassium fluorosilicate

The mixture of potassium hexafluorosilicate and zircon is fused at 700 °C and potassium hexafluorozirconate is obtained. The resulting mass is crushed, and then the fluoride salt is dissolved with acidified hot water. Filtration of the solution removes the silica and further cooling of the filtrate leads to the crystallisation of potassium hexafluorozirconate [2, 12, 16].

$$K_2SiF_6 + ZrSiO_4 \xrightarrow{600-700^\circ C} K_2ZrF_6 + 2SiO_2$$

Scheme 5.7: Reaction of zircon decomposition using potassium hexafluorosilicate as fondant [2, 16]

The product is milled and leached with a 1% hydrochloric acid solution at about 85°C for two hours. The saturated solution is filtered while hot to remove the silica, and potassium hexafluorozirconate crystallises as the solution cools [15, 16].

Potassium hexafluorosilicate is preferred to sodium hexafluorosilicate because of a lower tendency to dissociate and form silicon tetrafluoride by sublimation. Potassium chloride or carbonate can be added to the fusion product to promote completion of the reaction; they also reduce the tendency to dissociation of the potassium compound [15].

5.2.5 Fusion with calcium carbonate (or lime)

Lime (calcium oxide) or dolomite (a mineral that is a mixture of calcium carbonate and magnesium carbonate) can be used as a fondant. The resulting products are calcium zirconate and calcium and/or magnesium silicate. During the cooling process, the mass disintegrates into a very fine powder and coarse crystals of calcium zirconate. This difference enables the two to be separated by mechanical means. Since calcium zirconate is acid-soluble, it can be converted into a number of different chemicals or into zirconia [12, 19].

$$2ZrSiO_4 + 5CaCO_3 \rightarrow 2CaZrO_3 + (CaO)_3(SiO_2)_2 + CO_2$$
$$ZrSiO_4 + CaO + MgO \rightarrow CaO.MgO.SiO_2 + ZrO_2$$

Scheme 5.8: Reaction of zircon decomposition using calcium carbonate and oxides of magnesium and calcium as fondants

The second process is used on an industrial scale, while the first does not seem to have been attracted any commercial interest [48].

5.3 Chlorination

American and French zirconium metal producers are using this process. Chlorine is used as a fluidising gas and the reaction is endothermic. The energy required for the process is supplied via induction heating of the internal graphite walls of the chlorinator. The reaction takes place at 1 100 °C. The gases produced, consisting of zirconium tetrachloride, silicon tetrachloride and carbon monoxide, are cooled down to 200 °C [2, 12, 15, 48].

$$ZrSiO_4 + 4Cl_2 + 4C \rightarrow ZrCl_4 + SiCl_4 + CO$$

Scheme 5.9: Reaction of zircon carbochlorination

During the first cooling, zirconium tetrachloride, containing hafnium as impurity, is collected as a powder. Silicon tetrachloride is condensed following further condensation and is subsequently purified and used to produce fumed silica, fused quartz and fused quartz optical fibre [2, 12]. Currently, milled zircon and coke are chlorinated in fluidised beds using chlorine as fluidising medium [12, 15, 16].

Zirconium tetrachloride can be converted to oxychloride with water. Zirconium oxychloride can be crystallised by cooling the solution to 20 °C. This step allows major impurities to be separated out. The crystals can then be calcined to zirconia [16].

5.4 Carbiding Process

The process is done in an arc furnace, with the furnace being continuously fed from the top. In order to obtain complete vaporisation of the silicon monoxide and complete conversion of zircon to carbide, an insufficient quantity of carbon is used. The process can be summarised by the following reaction [12]:

$$ZrSiO_4 + 3C \xrightarrow{2500^{\circ}C} Zr(C, N, O) + SiO + 3CO$$

Scheme 5.10: Reaction of the zircon carbiding process

Zirconium carbonitride crude grows under the electrode, surrounded by unreacted mix, which acts as insulation for the steel furnace shell. The zirconium-containing product can be roasted in air to give a low-purity zirconia for use in refractories [2, 12].

The advantage of the process is that it is completely dry. There is, however, an environmental concern related to the airborne silica produced during the process. The alternative treatment consists of the chlorination of zirconium cyanonitride to zirconium tetrachloride [2, 12, 15].

5.5 Other Methods of Recovering Zirconia

Due to the high demand for zirconium and zirconium chemicals, new methods of recovering zirconia from zircon sands have been proposed by scientists. The following methods of zirconia recovery were found in a literature search.

5.5.1 Fusion with calcium sulphate

This method was proposed by Hanna [50]. The method is based on the thermal decomposition of calcium sulphate to calcium oxide. Temperatures varying from 900 °C to 1 400 °C were used, with a soaking period from 30 minutes to 3 hours.

The advantage of using calcium sulphate is that it decomposes to CaO and SO_2. Sulphur dioxide can be used to produce sulphuric acid. It appears to be a good process for countries with large sources of gypsum, the mineral of calcium sulphate [50].

5.5.2 Mechanical zirconia processing

Zircon is milled for long periods (100 to 340 hours) in a ball mill, with alkaline earth metal oxides [49, 50, 51]. As result, zirconia is released and the silica reacts with the alkaline earth metal oxides, according to the following reaction scheme:

$$MO + ZrSiO_4 \rightarrow MSiO_3 + ZrO_2 \qquad (a)$$

Scheme 5.11: Reaction scheme of the mechanical decomposition of zircon in the presence of alkaline earth metal oxides [49, 50, 51]

Here M represents the alkaline earth metals, namely magnesium, calcium, strontium and barium. The above scheme is consistent with a 1:1 mol ratio. When the ratio of alkaline earth metals is increased, parallel reactions occur:

$$MO + ZrO_2 \rightarrow MZrO_3 \quad (b)$$

$$MO + MSiO_3 \rightarrow M_2SiO_4 \quad (c)$$

Scheme 5.12: Mechanism of the mechanical decomposition reaction of zircon in the presence of alkaline earth metal oxides [49, 50, 51]

Reaction (a) is predicted to occur at 25°C. When magnesium is used, the free energies of (a) and (c) are similar, suggesting competition between the zircon and the metal metasilicate. A possible solution is to increase metal oxide amount to favour the formation of metal zirconates [51].

The hydroxide is less favourable than the oxides and the milling environment must be free of water. Although those reactions occur at room temperature, simply mixing zircon with these oxides does not produce any reaction. This can be explained either by negligible kinetic rates, related to the slow diffusion, or by the activation energy requirement [51].

Magnesium is the most appropriate alkaline metal oxide for this reaction because of its high solubility, and its low rates of hydration and carbonation [49].

5.5.3 Hydrothermal decomposition

The reaction is taken under autoclave conditions in aqueous media. Zircon is reacted with calcium hydroxide and sodium hydroxide. In the first stage, zircon reacts with sodium hydroxide according to following scheme of reaction:

$$ZrSiO_4 + 2NaOH \rightarrow Na_2ZrSiO_5 + H_2O$$

$$Na_2ZrSiO_5 + Ca(OH)_2 \rightarrow ZrO_2 + CaO.SiO_2.H_2O + 2NaOH$$

Scheme 5.13: Reaction scheme of zircon hydrothermal decomposition with calcium hydroxide in the presence of sodium hydroxide [52]

Sodium zirconium silicate reacts with calcium hydroxide to produce calcium silicate hydrates and zirconia, leaving unreacted sodium hydroxide, which plays a catalytic role in the reaction [52].

The resulting reaction includes only zircon and calcium hydroxide:

$$ZrSiO_4 + Ca(OH)_2 \rightarrow ZrO_2 + CaO.SiO_2.H_2O$$

Scheme 5.14: The overall reaction scheme of zircon hydrothermal decomposition with calcium hydroxide in the presence of sodium hydroxide [52]

The reaction is temperature-dependent. Increasing the reaction temperature has a positive effect on the reaction rate but above 100°C this also implies increased pressures [52].

The efficiency of the process reaches a maximum when the ratio of $Ca(OH)_2$:$ZrSiO_4$ equals 2 for a constant amount of sodium hydroxide. The size of the zircon particles influences the reaction strongly. The reaction is pH-dependent [52].

5.5.4 Anion-exchange process

Mohammed and Daher [53] proposed this decomposition process. Firstly sodium hydroxide is used to produce sodium zirconate and sodium silicate at 650°C. The cooled cake is leached with water and the wet residue digested in acid, filtered and washed in acid and then with demineralised water, and pH-adjusted. This solution was used for further experiments.

The zirconium solution is then passed through an anion-exchange resin to extract impurities of iron and uranium as complexes $[FeCl_4]^{2-}$ and $[UO_2Cl_4]^{2-}$. Zirconium is precipitated from the effluent as sulphate tetrahydrate. The sulphate is then calcined at 1 000 °C to zirconia [53]. The calcined residue consisted of high-purity zirconia.

5.6 Recovery of Zirconia from Baddeleyite

Although, on average, baddeleyite is composed of 80% by mass of zirconia, for certain applications complementary purification is needed. Several methods applied for baddeleyite purification are also used for zircon decomposition products.

5.6.1 Basic sulphate method

The US Bureau of Mines developed this method. It is based on the precipitation of zirconium basic sulphate. A constant acidity must be maintained during precipitation by dilution and the reaction temperature must be maintained at 39.5 °C. The acidity of the media increases due to the formation of free acid. If these conditions are met, then the yield can achieve values as high as 40% to 58%. The basic sulphate recovered in this way contains only traces of impurities [54].

The main difficulty in this process lies in controlling the acidity of the media as a result of the hydrolysis of zirconium sulphate with the formation of free sulphuric acid, according to the following reaction:

$$4Zr(SO_4)_2 + 19H_2O \rightarrow 4ZrO_2.3SO_3.14H_2O + 5H_2SO_4$$

Scheme 5.15: Reaction of the hydrolysis of zirconium sulphate in water during the processing of zirconium basic sulphate [54]

To overcome the problem, sulphuric acid is replaced by hydrochloric acid and soluble sulphates are added to provide sulphate ions. Sulphates of aluminium, sodium, magnesium and ammonium are used for this propose. With this alternative method, yields of around 97.5% can be achieved [54].

In another processing method, zirconyl sulphate solution is treated with sulphuric acid to give a mol ratio of zirconium to sulphate ions equal to 5:2. The solution is heated at 90 °C and diluted with water. At the same time, ammonium solution is added to keep the pH at 1.4. Basic zirconium sulphate, $Zr_5O_8(SO_4)_2.xH_2O$, is precipitated in over 99% yield. The precipitate is converted into hydroxide by refluxing with ammonia [54].

Zirconia or zircon is converted first to hydrous zirconia, then to zirconium oxychloride solution via reaction with hydrochloric acid. Sulphuric acid or ammonium sulphate is added to the zirconium oxychloride solution, followed by heating. Metallic impurities remain in the solution and need to be removed. However, some titanium remains because it is difficult to separate in this process. The sulphate is fired to zirconia [2, 12].

5.6.2 Oxychloride crystallisation

This method has been used, although it is considered to be too expensive because of the quantities of hydrochloric acid needed. It was used to produce zirconium oxychloride on a large scale. Traditionally, the product of chlorination of zircon or baddeleyite – zirconium tetrachloride contaminated with aluminium chloride, titanium tetrachloride, silicon tetrachloride and iron trichloride – is treated with 20% hydrochloric acid to produce zirconium oxychloride solution. The solution is gently heated to 65 °C. At this temperature, crystals start to form. The solution is allowed to stand for 24 hours and the temperature is kept above the crystallisation range by using hot water jackets [24, 54].

Crystals of zirconium oxychloride are dried at 85 °C and supplied for commercial use. To produce zirconia, zirconium oxychloride crystals are fired in air. A very hard and granular product is obtained. For fine zirconia, zirconium oxychloride is dissolved in water and ammonia is added to the precipitated zirconium hydroxide that is then fired to produce fine zirconia [54].

5.6.3 Precipitation with sulphur dioxide or sodium thiosulphate

This method is useful for producing zirconium compounds free from iron. Zirconium compounds hydrolyse much more readily than similar iron compounds. The precipitation of zirconium sulphate is hindered by the presence of sodium and potassium sulphates, but if these are present in only small amounts, the addition of sodium thiosulphate in excess will yield a good separation [54].

For successful precipitation with sodium thiosulphate, four conditions must be satisfied, namely:

- The solution must be only slightly acidic and relatively low in sodium and potassium.
- The solution should not be concentrated – a concentration of one part of zirconia to 50 parts of water is favourable.
- The addition of thiosulphate should be made to the solution heated to about 70 °C.
- After the addition of the thiosulphate solution, the solution should be allowed to stand for several hours to ensure complete precipitation.

For industrial use, it has been suggested that sulphur dioxide should be used to replace sodium thiosulphate, due to the large excess required, i.e. 500%. Sulphur dioxide is passed through a boiling solution of sodium zirconate diluted in hydrochloric acid. As a result, the zirconium precipitates completely [54].

5.6.4 Precipitation as phosphate

Zirconium phosphate is a useful compound for separating zirconium from other elements. It is insoluble in most strong mineral acids that retain most other elements in solution [54].

If hydrogen peroxide is added to the acid solution before the addition of phosphate ions, zirconium phosphate, unlike other phosphates, will still precipitate. The precipitate is, however, difficult to handle and the process will be difficult to operate on a large scale. There are some conditions to be followed [54]:

- The acidity of the hydrochloric or sulphuric acid solution of zirconium may vary from 3% to 20%.
- The solutions must be very dilute in relation to zirconium.
- The presence of hydrogen peroxide is essential to prevent the precipitation of titanium.
- The precipitation is hastened by heating or agitation.

Purity levels as high as 98% can be obtained. The process is referred to as being laborious and the result is not very satisfactory [54].

5.6.5 Purification as hydrated sulphate

The U.S. Bureau of Standards developed this method. The zirconium sulphate is claimed to be of a high purity, with a good yield [54]. In this process, zirconia or zircon is converted into a zirconate salt. The zirconate salt is hydrolysed and converted to sulphate or chloride zirconium solution. To that solution is added concentrated sulphuric acid. A crystalline white precipitate of zirconium sulphate, $Zr(SO_4)_2.4H_2O$, is formed. For purification, the crystals are dissolved in water, followed by reprecipitation of the hydrated sulphate. For the best results, one volume of sulphuric acid is added to two volumes of concentrated zirconium solution [2, 54].

5.6.6 Double fluorides procedure

Potassium zirconium fluoride may be prepared by dissolving zirconium oxide in hydrofluoric acid in lead vessels. Zirconium oxide that has been ignited at very high temperatures does not dissolve. After filtration, the solution is neutralised with a solution of pure potassium carbonate or hydroxide. Potassium zirconium fluoride precipitates as the solution cools down. The crystals are purified by recrystallisation [54].

It is difficult to separate impurities of titanium and iron by this method, and therefore repeated crystallisation to achieve a certain extent of separation is required and the starter zirconia material must be relatively pure. Titanium forms an analogous compound with the same solubility as the zirconium compound. Double fluoride prepared by this method had a purity of 99.99% [54].

5.6.7 Thermal decomposition of alkali chlorozirconates

Mixtures of zirconium tetrachloride and sodium chloride or potassium chloride are fused and decomposed by heating at 500 - 600 °C at atmospheric conditions. This has a double purpose. It physically traps the non-volatile matter and chemically binds those metal chloride impurities that can form alkali chloride double salts [54].

5.6.8 Sublimation of zirconium tetrafluoride

Zirconium tetrafluoride with high purity is prepared by the sublimation in vacuum of zirconium fluoride formed by the precipitation and dehydration method. The purification is achieved by sublimating zirconium tetrafluoride in hydrogen fluoride at 800 – 850 °C [12, 15, 54]. With high temperatures the impurities increase, but operating at lower temperatures slows the process of sublimation [54].

5.6.9 Mechanical processing

Using anhydrous zirconium tetrachloride as precursor, Dodd and McCormick [55] mixed it with lithium oxide and milled it for six hours in an inert atmosphere provided by an argon flux. After milling, the reactant mixture was heat-treated at 400 °C for 1 hour in the same inert atmosphere.

The lithium chloride by-product was removed by washing several times with deionised water and methanol in an ultrasonic bath. The powders were recovered by centrifugation. The powders were subsequently dried in air for several hours at 80 °C [55].

The proposed reaction for the process can be expressed in the following reaction scheme:

$$ZiCl_4 + 2Li_2O \rightarrow ZrO_2 + 4LiCl$$

Scheme 5.16: Reaction scheme of zirconium mechanical processing with lithium oxide [55]

Reaction between zirconium tetrachloride and lithium oxide occurs only after the low-temperature treatment. The reaction depends on the heating rate and also on the addition of lithium chloride as diluent. The addition of the diluent increases the size of the zirconia particles and thus reduces the average crystal size. This reduction is reported to favour the tetragonal phase [55].

Alternatively, magnesium oxide can be used and in this case the milling time is extended to 12 hours under the same conditions as for lithium oxide. The heat treatment must be conducted between 400 and 600 °C. The resulting reaction is shown in the following scheme [56]:

$$ZrCl_4 + 2MgO \rightarrow ZrO_2 + 2MgCl_2$$

Scheme 5.17: Reaction scheme of zirconium mechanical processing with magnesium oxide [56]

In the case of magnesium oxide, the reaction occurs during the milling process, unlike the reaction with oxides of calcium and lithium [56, 57], which needs supplementary heat for the reaction to take place. The reason for this difference is unknown [56].

The post-milling heat treatment is necessary to improve the crystallinity of the final zirconia powder. The zirconia produced is either tetragonal or cubic. The explanation for this is that the tetragonal phase has lower surface energy than the monoclinic phase, which is stable at ambient temperature. Thus a reduction in particle size to the nanometre regime can result in the stabilisation of high-temperature phases. However, it seems that this is not the real reason for the phenomenon [56].

5.6.10 Sodium metaphosphate method

This method is held to be appropriate for producing fully dense ceramics of uniform microstructure and thus consistent properties. These properties are desirable for mechanical and electrical applications [58].

In contrast to other process that involves solution precursors, this method avoids wet chemical processing. It produces tetragonal powders with approximately a particle size of 12 nm. This route is based on a solid-state reaction, at a relatively low temperature (500 °C), between sodium zirconate and sodium metaphosphate ($NaPO_3$). The reaction is represented by the following scheme:

$$Na_2ZrO_3 + NaPO_3 \rightarrow Na_3PO_4 + ZrO_2$$

Scheme 5.18: Reaction scheme of zirconia purification via the metaphosphate method [58]

The process produces sodium zirconate via the previously described processes of fusion. The reaction time ranges from 60 h to 100 h. For previous milled mixtures, 60 h is apparently sufficient [58].

5.7 Separation of Hafnium and Zirconium

Zirconium and hafnium are chemically and metallurgically very similar. They exhibit the same valences and have essentially the same ionic radii, 0.074 nm for Zr^{4+} and 0.075 for Hf^{4+}. For most uses, their separation is unnecessary. For nuclear power use, zirconium free of hafnium is necessary [12, 15].

The first method described by Coster and Hevesy uses fractional crystallisation of potassium or ammonium hexafluorozirconates [13]. Actually, four methods have been used industrially: fluoride salt crystallisation, methyl isobutyl ketone extraction, tributyl phosphate extraction and extractive distillation. Ion-exchange methods are also used for small-scale production [12, 13]. These methods are based on small differences in the equilibrium constants between zirconium and hafnium species. The use of differences in reaction rates has also been recommended [13].

5.7.1 Fluoride salt crystallisation

This consists of separating hafnium and zirconium by repeated crystallisation of hexafluorozirconate from hot aqueous solution. The solution is acidified to minimise oxide-fluoride salt formation. During each step the salt crystals are depleted of hafnium. This process has been used in the Ukraine [12].

5.7.2 Methyl isobutyl ketone extraction

This is based on the preferred extraction of hafnium dihydroxide thiocyanate from hydrochloric acid solution by methyl isobutyl ketone. This method was developed in the USA and is used by American producers [12, 15].

Zirconium-hafnium tetrachloride is dissolved in water to form dihydroxychlorides via hydrolysis in hydrochloric acid solution. The solution is mixed with methyl isobutyl ketone to extract iron as $HFeCl_4$ in the organic phase. Then ammonium thiocyanate is added to the dihydroxychloride solution. A mixture of dihydroxychloride and dihydroxythiocyanate of zirconium and hafnium is produced. The mixture is countercurrently mixed with methyl isobutyl ketone and thiocyanic acid solution to extract hafnium dihydroxide thiocyanate in the organic phase. Hafnium is recovered using dilute sulphuric acid in ketone solution [12, 15].

Zirconium is recovered from hydrochloric acid solution by heating the solution above 90 °C, adding precisely 2 mol of sulphuric acid for each 5 mol of zirconium and raising the pH carefully to 1.2 - 1.5 with dilute ammonium hydroxide. As a result, granular zirconium basic sulphate, $Zr_5O_8(SO_4)_2.xH_2O$, is precipitated. Zirconium basic sulphate is easily filtered and washed to remove aluminium and uranium impurities. The sulphate is mixed with ammonium hydroxide to convert it into hydrous zirconia, which is fired to produce pure zirconia [12, 15].

Organic reactants are recovered and reused. Considerable quantities of hydrochloric and sulphuric acid and ammonium are consumed. Zirconium produced via this process contains 35 - 90 ppm of hafnium. Hafnium contains 200 – 2 000 ppm of zirconium [12].

5.7.3 Tributyl phosphate extraction

This method was developed in France, Britain and the USA. It is used commercially in India to obtain zirconium for the nuclear industry. It has also been used commercially in the USA [12].

Hydrous zirconia and hafnia are dissolved in concentrated nitric acid. The solution is extracted countercurrently with tributyl phosphate solution in kerosene. Hafnium and most metallic impurities remain in the aqueous phase. Zirconium is recovered from the kerosene solution with dilute sulphuric acid solution, which causes it to precipitate, and it is then fired to pure zirconia [12].

5.7.4 Extractive distillation

Hafnium tetrachloride is slightly more volatile than zirconium tetrachloride. Thus, the two chlorides can be fractionally distilled if they are handled in the liquid state. This can be achieved by using a molten continuous solvent, $KCl\text{-}AlCl_3$, in which they are soluble. The distillation can therefore be conducted at atmospheric pressure [12, 15].

The mixture of zirconium-hafnium tetrachloride is heated above 437 °C, the triple point of zirconium tetrachloride. The hafnium tetrachloride and some zirconium tetrachloride are distilled. Pure zirconium tetrachloride remains [15].

5.8 Reduction to Metal

The first attempt to produce zirconium metal was made by Berzelius in 1824, using sodium-potassium hexafluorozirconate. The first pure zirconium was produced only in 1925, using the iodide thermal dissociation method [12, 15].

The reduction process is particularly difficult because of the strong tendency of zirconium to dissolve oxygen. Oxygen affects the properties of zirconium. Therefore, reducing agents must be oxygen-free, as well as nitrogen- and carbon-free [12, 15].

5.8.1 Kroll process

Zirconium metal is produced by reduction of zirconium tetrachloride with molten magnesium under inert conditions (argon or helium) [12].

Hafnium-free zirconia is mixed with pulverised coke and fed into an induction-heated chlorinator. The mixture is fluidised with chlorine gas. The reaction, at 900 °C, produces zirconium tetrachloride and carbon dioxide. Zirconium tetrachloride is collected in a nickel condenser below 200 °C, as a powder. Subliming and condensing again in a nitrogen-hydrogen atmosphere purifies the product. Such an atmosphere allows the reduction of the aluminium and phosphorus contents. The powder is placed in a cylindrical retort with magnesium casting ingots. The retort is repeatedly evacuated and filled with argon at 200 °C. Heat is then applied to the lower part of the retort to melt the magnesium ingots. Zirconium tetrachloride sublimes and is reduced to zirconium metal. Thereafter the retort is cooled down and unloaded. The bottom part of the reduced product contains “mud” – a thick suspension of tiny zirconium metal beads – under a layer of liquid magnesium chloride. Zirconium chloride is mechanically separated from the magnesium-zirconium metallic regulus [12, 15].

The regulus is then distilled to remove residual magnesium chloride and magnesium metal. At 980 °C magnesium chloride melts and is drained, while magnesium metal is condensed on the cold wall of the lower retort. Zirconium metal begins to sinter together. The porous mass obtained is known as zirconium sponge [12, 15].

5.8.2 Other reduction processes

Ductile zirconium has been commercially produced in a two-step sodium reduction of zirconium tetrachloride. In the first stage of the process, zirconium tetrachloride in vapour is continuously fed into a stirred argon-filled reactor containing sodium chloride. Zirconium tetrachloride is reduced to zirconium dichloride via the sodium. This step is very exothermic and the heat release rate determines the feed rate [12, 15].

The $ZrCl_2$-NaCl is transferred to a second reactor where the mixture is reheated with additional sodium. As a result, zirconium dichloride is reduced to zirconium metal. Sodium chloride is removed by leaching with water [12, 15].

The reduction can be achieved by using potassium hexafluorozirconate with calcium metal in a sealed bomb. This process is used in Russia. With calcium, zirconium tetrachloride can also be used [12, 15].

Zirconia can also be reduced with calcium or magnesium. Finely divided zirconium metal is recovered by leaching with cold hydrochloric acid. The powder is very pyrophoric due to the large surface area. The powder contains 0.3 - 0.5% of oxygen, so it cannot be malleable and ductile if melted in ingots [12, 15].

5.8.3 Electrolysis

This process has been considered as an alternative to the Kroll process, but it is difficult. Using only a chloride salts system is inefficient due to the lower stability of the chlorides in the melts. Adding a small amount of fluorine salts increases the stability of zirconium (IV) ions in solution, decreasing the concentration of the lower-valence zirconium ions. This raises the efficiency of the current [12, 15].

5.9 Refining

Kroll zirconium is pure and ductile for most applications. But for some other applications in which extremely soft metal is needed and, for research studies, further purification is required. Purification is achieved by the van Arkel-de Boer method, also called the "iodide-bar process". The van Arkel-de Boer process was the only one used from 1925 to 1945 to produce pure zirconium from zirconium ores. Nowadays, the method is only used only to produce zirconium of high purity [12, 15].

Iodide vapour is reacted with Kroll zirconium sponge or calcium-reduced metal powder to produce zirconium tetraiodide. Zirconium tetraiodide vapour diffuses to a heated filament, usually zirconium wire, where it is thermal dissociated, depositing zirconium and releasing iodine to be recycled [12, 15].

$$2I_2 + Zr \xrightarrow{250\text{-}300°C} ZrI_4 \xrightarrow{1200\text{-}1500°C} Zr + 2I_2$$

Scheme 5.19: Reaction scheme of zirconium refining process [12, 15]

The diameter of the filament grows as zirconium is deposited. Bars up to 40-50 mm in diameter can be grown from a zirconium filament 3 mm in diameter [12, 15].

Electron beam melting of zirconium has been used to remove more volatile impurities, such as iron and aluminium. This method is not usually used because the metal's vapour pressure at its melting point is higher than that of most impurities. The metal vapour pressure results in considerable losses in the high vacuum utilised in electron beam melting [12, 15].